

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE  
(03259.81130)**

**Applicants:** Schwertfeger et al.

**U.S. Serial No.:** Continuation of USSN 09/308,888

**Group Art Unit:** 1712

**Filed:** On Even Date Herewith

**Examiner:** Lovering, R.

**Title:** Organically Modified Aerogels, Method for Their Production by Surface Modification of the Aqueous Gel Without Previous Solvent Exchange and Subsequent Drying and the Use Thereof

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Assistant Commissioner for Patents, Box Patent Application  
Washington, DC 20231

**PRELIMINARY AMENDMENT**

Sir:

Please amend the above-identified application as follows:

**IN THE SPECIFICATION:**

Please insert the following sentence at page 1 as the first sentence of the Specification, above the heading "Description":

--This application is a continuation of United States Patent Application No. 09/308,888 which is United States National Phase Application under 35 U.S.C. § 371 of PCT/EP97/06595 filed on November 26, 1997.--

On page 7 of the specification after line 17, please insert and center the following:

--Brief Description of the Drawings--

After "Brief Description of the Drawings" please insert the following:

--FIG 1 shows aerogel particles; and  
FIG 2 shows a view of NaCl crystals in an aerogel monolith using a scanning electron microscope.--

Support for the descriptions of the figures may be found throughout the specification specifically, for example, on page 26, lines 14-26 of the specification.

## IN THE CLAIMS

Please amend claims as follows:

Claim 3. (Amended) Method for the production of organically modified aerogels, characterized in that:

- a) a silicatic hydrogel is formed at  $\text{pH} \geq 3$ ;
- b) the silicatic hydrogel formed in step a), optionally after intermediate treatment steps, is subjected to surface modification by mixing the hydrogel with hydrophobing agent to form a surface modified gel;
- c) the surface modified gel obtained in step b), optionally after additional treatment steps, is dried,

wherein the silicatic hydrogel is prepared by bringing an aqueous waterglass solution to a pH  $\leq 3$  with the aid of an acidic ion exchanger resin, a mineral acid, polycondensing the resulting silicic acid by addition of a base to form an  $\text{SiO}_2$  gel, and, if desired, washing the gel with water to free it from any electrolyte.

Claim 5. (Amended) Method for the production of organically modified aerogels, characterized in that:

- a) a silicatic hydrogel is formed at pH  $\geq 3$ ;
- b) the silicatic hydrogel formed in step a), optionally after intermediate treatment steps, is subjected to surface modification by mixing the hydrogel with hydrophobing agent to form a surface modified gel;
- c) the surface modified gel obtained in step b), optionally after additional treatment steps, is dried,

wherein the silicatic hydrogel is obtained by hydrolysis and polycondensation of silicon tetrachloride..

Claim 6. (Amended) The process as claimed in claim 2, wherein additives are added before and/or during the preparation of the gel.

Claim 8. (Amended) The process according to claim 1, wherein the hydrogel obtained in step a) is aged before being surface-modified in step b).

Claim 9. (Amended) The process according to claim 1, wherein the hydrogel obtained in step b) is subjected to surface silylation using a silylating agent.

Claim 16. (Amended) The process as claimed in claim 13, wherein the silylating agent employed is hexamethyldisiloxane.

Claim 17. (Amended) The process as claimed in claim 1, wherein at least one acid and/or base is introduced as initial charge in the hydrogel before surface modification.

Claim 19. (Amended) The process as claimed in claim 9, wherein the hydrogel is introduced as initial charge in the silylating agent, and then at least one acid and/or base is added.

Claim 22. (Amended) The process as claimed in claim 1, wherein the agent for surface modification is generated shortly before and/or during the surface modification, preferably by means of an acid.

Claim 23. (Amended) The process as claimed in claim 1, wherein the surface modification is accelerated by means of a catalyst.

Claim 24. (Amended) The process as claimed in claim 1, wherein at least one carrier gas or carrier gas stream is used in step b) in addition to the agent for surface modification.

Claim 25. (Amended) The process as claimed in claim 1, wherein some of the water in pores of the hydrogel reacts with the surface modification agent to form a water-insoluble compound.

Claim 27. (Amended) The process as claimed in claim 1, wherein an outer surface of the hydrogel is dried prior to surface modification.

Claim 31. (Amended) The process as claimed in claim 1, wherein the surface-modified gel is washed with a protic or aprotic solvent prior to step c).

Claim 32. (Amended) The process as claimed in claim 1, wherein the surface-modified gel is washed with a silylating agent prior to step c).

Claim 33. (Amended) The process as claimed in claim 1, wherein the surface-modified gel is subjected to subcritical drying in step c).

Claim 34. (Amended) The process as claimed in claim 2, wherein the gel obtained in step a) is reacted, prior to silylation, with a solution of a condensable orthosilicate of the formula  $R^1_{4-n}Si(OR^2)_n$ , preferably an alkyl and/or aryl orthosilicate, where  $n = 2$  to  $4$  and  $R^1$  and  $R^2$  independently of one another are hydrogen atoms or linear or branched  $C_1$ - $C_6$  alkyl, cyclohexyl or phenyl radical, or with an aqueous silicic acid solution.

Claim 35. (Amended) The process as claimed in claim 1, wherein surface modification is carried out in the presence of additives in the hydrogel.

Claim 39. (Amended) An aerogel whose internal surface is covered by at least 90% of the theoretically possible value with organic surface groups which have been applied by surface modification.

Claim 42. (Amended) An aerogel as claimed in claim 41, which comprises ionic compounds as additives.

Claim 43. (Amended) The aerogel as claimed in claim 41, which comprises opacifiers as additives.

Claim 44. (Amended) The aerogel as claimed in claim 41 which comprises fibers as additives.

Claim 45. (Amended) The aerogel as claimed in claim 41, which has a BET internal surface area of less than  $600 \text{ m}^2/\text{g}$ .

Claim 46. (Amended) The aerogel as claimed in claim 41, which has a thermal conductivity of  $< 12 \text{ mW/mK}$ .

Claim 47. (Amended) The aerogel as claimed in claim 38, which is based on silicate.

Claim 48. (Amended) The use of an aerogel as claimed in claim 38 as a thermal insulation material.

Claim 51. (Amended) A lyogel whose internal surface is covered, by at least 90% of the theoretically possible value, with organic surface groups which have been applied by surface modification.

Claim 53. (Amended) The use of a lyogel as claimed in claim 50 or 51 in chromatography, in cosmetology and in the pharmaceuticals sector.

Please add following new claims 54-66:

--54. (NEW) Method for the production of organically modified aerogels, characterized in that:

- a) a hydrogel is formed at  $\text{pH} \geq 3$ ;
- b) the hydrogel formed in step a), optionally after intermediate treatment steps, is subjected to surface modification by mixing the hydrogel with hydrophobing agent to form a surface modified gel;

c) the surface modified gel obtained in step b), optionally after additional treatment steps, is dried. --

--55. (NEW) The method for the production of organically modified aerogel according to claim 54, characterized in that the hydrogel is formed in step a) at pH between pH 3 and pH 8.--

--56. (NEW) The method for the production of organically modified aerogel according to claim 54 or 55, characterized in that the hydrogel is formed in step a) by lowering the pH of an aqueous waterglass solution.--

--57. (NEW) The method for the production of organically modified aerogel according to claim 55, characterized in that the pH of an aqueous waterglass solution is lowered in step a) to a pH value not less than 3. --

--58. (NEW) Method for the production of organically modified aerogels characterized in that a) a hydrogel is formed by lowering the pH of an aqueous waterglass solution by addition of acid to  $\text{pH} \geq 8$  and establishing the pH between pH 3 and pH 8; b) the hydrogel formed in step a) optionally after intermediate treatment steps, is subjected to surface modification by mixing the hydrogel with hydrophobing agent to form a surface modified gel; and c) the surface modified gel obtained in step b), optionally after additional treatment steps, is dried.--

--59. (NEW) The method for the production of organically modified aerogel according to claim 54 or 55, characterized in that the hydrogel is formed in step a) by addition of acid to aqueous waterglass solution and without subsequent addition of base in step a).--

--60. (NEW) The method for the production of organically modified aerogel according to claim 54 or 55, characterized in that step a) and b) are carried out as a semi-continuous process.--

--61. (NEW) The method for the production of organically modified aerogel according to claim 54 or 55, characterized in that steps a) and b) are carried out as a continuous process.--

--62. (NEW) The method for the production of organically modified aerogel according to claim 60 or 61, characterized in that a continuous or semi-continuous stream of acid is mixed with a continuous or semi-continuous stream of aqueous waterglass solution.--

--63. (NEW) The method for the production of organically modified aerogel according to claim 62, characterized in that the acid stream is admixed with the aqueous waterglass solution through a mixing nozzle.--

--64. (NEW) The method for the production of organically modified aerogel according to claim 54, wherein step b) results in a hydrophobic gel in a liquid phase substantially immiscible with water, which liquid is separated from an aqueous phase formed by the water from the hydrogel.--

--65. (NEW) The method for the production of organically modified aerogel according to claim 11, characterized in that the hydrophobing agent comprises at least TMCS and the liquid phase comprises at least HMDSO.--

--66. (NEW) The method for the production of organically modified aerogel according to claim 12, characterized in that at least a portion of the HMDSO is subsequently recycled.--



**REMARKS**

Upon entry of the foregoing amendments, claims 1-66 are pending in the application. Support for new claims 54-66 is found throughout the specification and claims as originally filed. Support for independent claim 54 is found, for example, at pages 7-13 (step a) and the Examples of the specification. More specifically, support for step (a) of claim 54 which recites "a hydrogel is formed at  $\text{pH} \geq 3$ " may be found, e.g. on page 9, lines 24-30. The specification discloses (page 9, lines 25-26) "...add some of the acid to the waterglass solution until a  $\text{pH} \geq 8$  is obtained" and then "... to establish the abovementioned pH of the sol..." (page 9, lines 26-27). The "abovementioned pH of the sol" refers to the pH achieved by adding base to a sol having pH 3 (or below) disclosed at page 7, lines 22-26. Adding base to a solution which is previously at pH 3 can only raise the pH of the solution to a  $\text{pH} \geq 3$ . Support for step (b) of claim 54 may be found on pages 13-24. Such disclosure includes, for example, the statement on page 13, line 25, "the hydrogel formed in step a) may be surface modified..." Support for step (c) of claim 54 may be found on pages 24-29. Such disclosure includes, for example, the statement on page 24, lines 1-2, "In step c) the silylated and possibly washed gel is subjected to preferably subcritical drying."

Support for claims 55-59 is found, for example, in the disclosure cited above and on page 9, lines 24-30 and in the Examples. Such disclosure includes "forming a hydrogel at pH between pH 3 and pH 8 and establishing the pH between pH 3 and pH 8" (page 9, lines 24-29) without subsequent addition of base (Examples). Support for claims 60-63 is found, for example, on page 9, lines 22-34 to page 10, lines 1-10. Such disclosure includes "mixing acid and waterglass (page 9, line 24) ... preferably in a semi-continuous or continuous process" (page 10, line 9) using, for example, a mixing nozzle (page 10, line 10). Support for claims 64 and 66 can be found on page 22, lines 29-34 to page 23, lines 1-13. Such disclosure includes formation of a liquid phase substantially immiscible with water (page 22, line 29-32) and recycling HMDSO (page 23, lines 3-10). Support for claim 65

can be found on page 18, lines 12-23. Such disclosure includes a hydrophobing agent which comprises TMCS and HMDSO (page 18, lines 15-20).

Attached hereto as Attachment A is a marked-up version of the changes made to the claims by the current Preliminary Amendment. The attachment is captioned **"Version With Markings To Show Changes Made."**

Please charge any fees due in connection with this Preliminary Amendment or the addition of claims made herein to Deposit Account No. 19-0733.

Respectfully submitted,

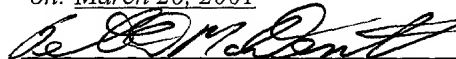


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Peter D. McDermott

3/26/01  
Date

**ATTACHMENT A**  
**VERSION WITH MARKINGS TO SHOW CHANGES MADE**

**IN THE CLAIMS:**

Claims 3, 5, 6, 8, 9, 16, 17, 19, 22-25, 27, 31-35, 39, 42-48, 51, and 53 have been amended as follows:

Claim 3. (Amended) [The process as claimed in claim 2] Method for the production of organically modified aerogels, characterized in that:

- a) a silicatic hydrogel is formed at  $\text{pH} \geq 3$ ;
- b) the silicatic hydrogel formed in step a), optionally after intermediate treatment steps, is subjected to surface modification by mixing the hydrogel with hydrophobing agent to form a surface modified gel;
- c) the surface modified gel obtained in step b), optionally after additional treatment steps, is dried,

wherein the silicatic hydrogel [introduced as initial charge in step a)] is prepared by bringing an aqueous waterglass solution to a  $\text{pH} \leq 3$  with the aid of an acidic ion exchanger resin, a mineral acid [or a hydrochloric acid solution], polycondensing the resulting silicic acid by addition of a base to form an  $\text{SiO}_2$  gel, and, if desired, washing the gel with water to free it from any electrolyte.

Claim 5. (Amended) [The process as claimed in claim 2] Method for the production of organically modified aerogels, characterized in that:

- a) a silicatic hydrogel is formed at  $\text{pH} \geq 3$ ;

b) the silicatic hydrogel formed in step a), optionally after intermediate treatment steps, is subjected to surface modification by mixing the hydrogel with hydrophobing agent to form a surface modified gel;

c) the surface modified gel obtained in step b), optionally after additional treatment steps, is dried,

wherein the silicatic hydrogel [introduced as initial charge in step a)] is obtained by hydrolysis and polycondensation of silicon tetrachloride.

Claim 6. (Amended) The process as claimed in [at least one of ] claim[s] 2 [to 5], wherein additives are added before and/or during the preparation of the gel.

Claim 8. (Amended) The process according to [as claimed in at least one of the preceding] claim[s] 1, wherein the hydrogel obtained in step a) is aged before being surface-modified in step b).

Claim 9. (Amended) The process according to [at least one of the preceding] claim[s] 1, wherein the hydrogel obtained in step b) is subjected to surface silylation using a silylating agent.

Claim 16. (Amended) The process as claimed in [at least one of] claim[s] 13 [to 15], wherein the silylating agent employed is hexamethyldisiloxane.

Claim 17. (Amended) The process as claimed in [at least one of the preceding claims] claim 1, wherein at least one acid and/or base is introduced as initial charge in the hydrogel before surface modification.

Claim 19. (Amended) The process as claimed in [at least one of the preceding] claim[s] 9, wherein the hydrogel is introduced as initial charge in the silylating agent [or agents], and then at least one acid and/or base is added.

Claim 22. (Amended) The process as claimed in [at least one of the preceding claims] claim 1, wherein the agent for surface modification is generated shortly before and/or during the surface modification, preferably by means of an acid.

Claim 23. (Amended) The process as claimed in [at least one of the preceding claims] claim 1, wherein the surface modification is accelerated by means of a catalyst.

Claim 24. (Amended) The process as claimed in [at least one of the preceding claims] claim 1, wherein at least one carrier gas or carrier gas stream is used in step b) in addition to the agent for surface modification.

Claim 25. (Amended) The process as claimed in [at least one of the preceding claims] claim 1, wherein some of the water in [the] pores of the hydrogel reacts with the surface modification agent to form a water-insoluble compound.

Claim 27. (Amended) The process as claimed in [at least one of the preceding claims] claim 1, wherein [the] an outer surface of the hydrogel is dried prior to surface modification.

Claim 31. (Amended) The process as claimed in [at least one of the preceding claims] claim 1, wherein the surface-modified gel is washed with a protic or aprotic solvent prior to step c).

Claim 32. (Amended) The process as claimed in [at least one of the preceding claims] claim 1, wherein the surface-modified gel is washed with a silylating agent prior to step c).

Claim 33. (Amended) The process as claimed in [at least one of the preceding claims] claim 1, wherein the surface-modified gel is subjected to subcritical drying in step c).

Claim 34. (Amended) The process as claimed in [at least one of] claim[s] 2 [to 33], wherein the gel obtained in step a) is reacted, prior to silylation, with a solution of a condensable orthosilicate of the formula  $R^1_{4-n}Si(OR^2)_n$ , preferably an alkyl and/or aryl orthosilicate, where  $n = 2$  to 4 and  $R^1$  and  $R^2$  independently of one another are hydrogen atoms or linear or branched  $C_1$ - $C_6$  alkyl, cyclohexyl or phenyl radical, or with an aqueous silicic acid solution.

Claim 35. (Amended) The process as claimed in [one of the preceding claims] claim 1, wherein surface modification is carried out in the presence of additives in the hydrogel.

Claim 39. (Amended) An aerogel [the degree of coverage of] whose internal surface is covered by at least 90% of the theoretically possible value with organic surface groups which have been applied by surface modification [,preferably surface silylation, is at least 90% of the theoretically possible value].

Claim 42. (Amended) An aerogel as claimed in claim 41, which comprises ionic compounds [, preferably NaCl,] as additives.

Claim 43. (Amended) The aerogel as claimed in claim 41 [or 42], which comprises opacifiers [, preferably IR opacifiers,] as additives.

Claim 44. (Amended) The aerogel as claimed in [any of claims] claim 41 [to 43] which comprises fibers as additives.

Claim 45. (Amended) The aerogel as claimed in [at least one of claims] claim 41 [to 44], which has a BET internal surface area of less than  $600 \text{ m}^2/\text{g}$  [,preferably less than  $500 \text{ m}^2/\text{g}$ ].

Claim 46. (Amended) [An] The aerogel as claimed in claim 41, which has a thermal conductivity of  $< 12 \text{ mW/mK}$ .

Claim 47. (Amended) The aerogel as claimed in [at least one of] claim[s] 38 [to 46], which is based on silicate.

Claim 48. (Amended) The use of an aerogel as claimed in [at least one of] claim[s] 38 [to 47] as a thermal insulation material.

Claim 51. (Amended) A lyogel [the degree of coverage of] whose internal surface is covered, by at least 90% of the theoretically possible value, with organic surface groups which have been applied by surface modification [,preferably surface silylation, is at least 90% of the theoretically possible value].

Claim 53. (Amended) The use of a lyogel as claimed in [at least one of] claim[s] 50 [to 52] or 51 in chromatography, in cosmetology and in the pharmaceuticals sector.